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14. ABSTRACT Fundamental developments in this project include (1) an analytic theory of pooling of infrared quanta on surfaces, with a potential application to laser-selective chemistry, (2) diffusion-electron transfer reaction rate theory for intermittent fluorescence of semiconductor nanoparticles, explaining the power law distribution of bright and dark periods and the exponential tail for bright periods, (3) theory of intermittent fluorescence of dyes on semiconductor nanoparticles and plane surfaces, (4) approximate semiclassical instanton theory for H-tunneling in small and large					
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Report Title

Fundamentals of Chemistry at Surfaces and Beyond

ABSTRACT

Fundamental developments in this project include (1) an analytic theory of pooling of infrared quanta on surfaces, with a potential application to laser-selective chemistry, (2) diffusion-electron transfer reaction rate theory for intermittent fluorescence of semiconductor nanoparticles, explaining the power law distribution of bright and dark periods and the exponential tail for bright periods, (3) theory of intermittent fluorescence of dyes on semiconductor nanoparticles and plane surfaces, (4) approximate semiclassical instanton theory for H-tunneling in small and large systems, computationally less demanding than more accurate approaches and whose utility is being explored, and (5) marked improvement of the range of validity of the maximum likelihood method so as to treat power law data, converging when the common method diverges.

The theory of infrared quanta pooling (accumulation of quanta in individual adsorbed molecules on surfaces) rapid equilibration of the quanta was assumed among the sites and the results were compared with a kinetic Monte Carlo computational solution of the coupled kinetic differential equations. When the assumption is valid (high light intensities), the theory has applications to infrared laser selective chemistry on surfaces. Research has also been initiated on a fundamental electron transfer theory for perovskite-like and other photovoltaic solar cells.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
03/21/2012	4.00 Rudolph A. Marcus. At the Birth of Modern Semiclassical Theory, Molecular Physics, (03 2012): 0. doi:
07/26/2012	6.00 R. A. Marcus, Zhaoyan Zhu. A Maximum Likelihood Method for Power Law Distributions That Does Not Break Down When the Slope Is Close to Unity, The Journal of Physical Chemistry C, (06 2012): 14690. doi: 10.1021/jp303697j
07/26/2012	5.00 Wei-Chen Chen, R. A. Marcus. Theory of a Single Dye Molecule Blinking with a Diffusion-Based Power Law Distribution, The Journal of Physical Chemistry C, (06 2012): 0. doi: 10.1021/jp303837g
07/28/2011	2.00 Nathan O. Hodas, Yousung Jung, Yanting Wang, R. A. Marcus. Microscopic structure and dynamics of air/water interface by computer simulations—comparison with sum-frequency generation experiments, Physical Chemistry Chemical Physics, (02 2011): 0. doi: 10.1039/c0cp02745f
08/04/2011	3.00 Maksym Kryvohuz. Semiclassical instanton approach to calculation of reaction rate constants in multidimensional chemical systems, Journal of Chemical Physics, (03 2011): 0. doi:
09/17/2013	13.00 . Theory of Vibrational Equilibria and Pooling at Solid-Diatom Interfaces, J Chem Phys, (09 2013): 0. doi:
09/20/2013	15.00 David M. Wardlaw, R.A. Marcus. Historical Perspective: RRKM Reaction Rate Theory for Transition States of Any Looseness [Volume 110, Issue 3, 28 September 1984, Pages 230–234], Chemical Physics Letters, (08 2013): 0. doi: 10.1016/j.cplett.2013.08.041
TOTAL:	7

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
02/27/2013	10.00 R.A. Marcus. Electron Transfer Theory and its Inception, Phys. Chem. Chem. Phys., (08 2012): 13729. doi:
02/27/2013	9.00 M. Kryvohuz, R.A. Marcus. Semiclassical Evaluation of Kinetic Isotope Effects in 13-Atomic System, Journal of Chemical Physics, (10 2012): 134107. doi:
TOTAL:	2

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Lecture: Electron Transfer Reactions in Chemistry, Physics Club, Westridge High School, Pasadena, CA, 2012
Lecture: Electron Transfers and Other Reactions in Chemistry, Baku State University, Azerbaijan, 2012
Conference Lecture: Single Molecule Studies in Initial Steps in Dye Sensitized Solar Cells and in Quantum Dots - Examples of Electron Transfers, 19th International Conference on Photochemical Conversion and Storage of Solar Energy, California Institute of Technology, Pasadena, CA, 2012
Plenary Lecture: Electron Transfer Reaction Theory in Chemistry - from the Isotopic Exchange Reactions of the 1940s and 1950s to the Modern Solar Energy Conversion Era, International Conference on Recent Advances in Materials Science, Bangalore, India, 2012
Lecture: From Experiment to Theory to Experiments - Electron Transfer Reactions in Chemistry, Tumkur University, Tumkur, India, 2012
Lecture: Electron Transfer Reaction Theory in Chemistry - from the Isotopic Exchange Reactions of the 1940s and 1950s to the Modern Solar Energy Conversion Era, Indian Institute of Science Bangalore, Bangalore, India, 2012
Lecture: Electron Transfer Reactions, H Transfers in Enzymes, and "On-Water" Reactions, National Centre for Biological Sciences, Bangalore, India, 2012
Lecture: Electron Transfer Reactions, H Transfers in Enzymes, and "On-Water" Reactions, University of Hyderabad, Hyderabad, India, 2012

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

<u>Received</u>	<u>Paper</u>
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09/17/2013	14.00	E. T. D. Boney, R. A. Marcus. On the Infrared Fluorescence of Monolayer $^{13}\text{CO}:\text{NaCl}(100)$, J Chem Phys (submitted) (08 2013)
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TOTAL: 1

Number of Manuscripts:

Books

<u>Received</u>	<u>Paper</u>
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TOTAL:

Patents Submitted

Patents Awarded

Awards

Honorary Doctor of Science, Tumkur University, India, 2012
Honorary Doctor of Science, University of Hyderabad, India, 2012

Postage Stamp, Ghana, 2013

The Prof. Rudolph A. Marcus Award, Journal of Spectroscopy and Dynamics, 2013

Conference in Honour of the 90th Birthday of Rudolph Marcus, Nanyang Technological University, Singapore, 2013

Honorary Doctor of Laws, University of Calgary, Canada 2013

John G. Kirkwood and Arthur A. Noyes Professor of Chemistry, California Institute of Technology

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Evans Boney	0.14	
Yun-Hua Hong	0.10	
FTE Equivalent:	0.24	
Total Number:	2	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	
Wei-Chen Chen	0.15	
Sandor Volkan-Kacso	0.13	
Zhaoyan Zhu	0.72	
FTE Equivalent:	1.00	
Total Number:	3	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Rudolph A. Marcus (PI)	0.12	Yes
FTE Equivalent:	0.12	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	
FTE Equivalent:		
Total Number:		

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>

Total Number:

Names of personnel receiving PhDs

<u>NAME</u>

Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Maksym Kryvohuz	0.10
FTE Equivalent:	0.10
Total Number:	1

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachments. Incidentally, two publications listed in an earlier report as being non peer-reviewed were reviewed.

Technology Transfer

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Statement of the Problem

This research is aimed at understanding fundamental processes such as accumulation of vibrational quanta in molecules adsorbed on surfaces, with a view to application to infrared laser selective chemistry, and understanding the behavior of other surface-focused systems ranging from electron transfer in semiconductor nanoparticles, as revealed in their intermittent fluorescence, to phenomena related to photovoltaic solar cells and catalysis of chemical reactions at liquid interfaces involving water. Analytic theory, and its interaction with experiment and computations plays a key role in this research. The current findings of the research performed with this grant support are summarized and publications are included.

The Most Important Results

- An analytic theory was given for vibrational pooling of molecules on solid surfaces. The theory has application to infrared laser selective chemistry on surfaces, for example, to the recent strange history of such chemistry on a hydrogen-terminated silicon surface, a passivated surface important because of its enhanced stability in ambient environments. SECTION A.1
- A diffusion controlled electron transfer theory was given for the intermittent fluorescence of semiconductor nanoparticles that incorporates for the first time the main quantitative features of the phenomenon: a power law for the distribution of light and dark periods that is usually centered on -1.5 complemented by an explanation of why only dark periods have a “simple” power law but the light periods have a power law plus an exponential tail. The extensive studies of the optical properties of semiconductor nanoparticles in the literature is prompted by their use in biological sensing, photovoltaic devices, electro-chemiluminescent displays, and solid state lighting. SECTION B.1
- A theory for the intermittent fluorescence of dye molecules on semiconductor surfaces was developed that is based on diffusion controlled electron transfer. This theory accounts for the -1.0 power law for the distribution of dark states after photoinjection of electrons from the excited dye molecules into a semiconductor. The theory provides also an answer to the question why the same behavior can occur also for the light periods. Then, electron transfer is from excited dye molecules to defect surface states located within the band gap of the semiconductor

instead of electron injection into its conduction band. This concept is new and covers hitherto unexplained observations in the field of organic/inorganic solar photovoltaics. SECTION B.2

- We developed the methodology in the maximum likelihood theoretical treatment, of power law data for surfaces. In particular we devised a maximum likelihood method that, unlike a conventional method in the literature, has no singularity. We applied the result to single molecule experiments for photo injection of electrons from dyes into surfaces. SECTION B.3
- A semiclassical instanton method for studying kinetic isotope effects in reactions was simplified, a subsequent development being the use of potential energy surfaces “on the fly”. SECTION C

Several works of this project show the power of analytic treatments, in their own right, and in their interaction with computations and with experiments.

Fundamentals of Chemistry at Surfaces and Beyond

A. Infrared Laser Selective Chemistry

A1. Analytic Theory for Infrared Pooling and Tests of Theory

This research is aimed at understanding fundamental processes such as accumulation of vibrational quanta in molecules adsorbed on surfaces, with a view to application to infrared laser selective chemistry, and understanding the behavior of other surface-focused systems ranging from electron transfer in semiconductor nanoparticles, as revealed in their intermittent fluorescence, to phenomena related to photovoltaic solar cells and catalysis of chemical reactions at liquid interfaces involving water. Analytic theory, and its interaction with experiment and computations plays a key role in this research. The current findings of the research performed with this grant support are summarized and publications are included.

The question of infrared laser selective chemistry has been and still is a subject of much interest. During the course of this research we have developed an analytic theory of pooling of infrared quanta of an adsorbate on a surface¹ permitting an understanding of the experimental data and the results of our and others’ numerical computations. In the theory one obtains the population of vibrational states of the adsorbate molecules. To this end we used statistical mechanics, letting the system equilibrate among the vibrational states of the adsorbate at each time t . This assumption of vibrational equilibration amounted to assuming that pooling (accumulation of quanta on individual adsorption sites) and depooling are fast relative to all other processes, such as loss of quanta to the solid. We also assumed that only one-quantum exchanges occur between adsorbed molecules and that the energy transfer between the adsorbate and the solid is limited in pooling by the physics-based assumption of not having a transfer of a quantum larger than the vibrational quantum corresponding to the Debye frequency cut-off of the solid. The latter provides a key difference from pooling² in the gas phase.

We then calculated and minimized the free energy of the adsorbate, subject to these constraints. We obtained the distribution of vibrational states of the adsorbate, an inverted distribution rather

than a Boltzmann distribution, and tested the theory by comparing this statistical result with our numerical solution of the “master equation”. The latter is a set of many coupled kinetic ordinary differential equations for the vibrational population of the different sites on the surface, describing the many processes that occur between the quantum states of the adsorbate molecules, between these quantum states and the solid, and for the loss of energy by fluorescence of the adsorbed molecules.

The numerical solution of these coupled differential equations was obtained using a kinetic Monte Carlo integration, using an earlier procedure in the literature^{3,4}. We then compared the numerical results with the existing experimental data⁵ and with our analytic theory. An ultimate goal is to combine this theory for pooling with a theory for chemical reactions on the surface, and use the overall theory to predict when infrared laser selective chemistry for adsorbates on solids can occur and when it cannot. A second goal was to explain why the kinetic results were a single exponential decay⁵, even though there are numerous first and second order kinetic processes occurring. The answer, we showed, is a rapid equilibration among the vibrational states of the adsorbed molecules. There have been recent uncertain experiments on laser selective chemistry in this field⁶, and a goal of the theory is to point to conditions for new experiments that can explore this issue. This work is ongoing. The first paper in this series will appear in an October issue of the Journal of Chemical Physics.

A2. Infrared Laser Selective Desorption of H₂ from an Si-H Surface

In the context of infrared laser selective chemistry a *Science* paper⁶ appeared on infrared laser-selective desorption of H₂ from an Si-H surface in the presence of excess Si-D. Since the experimental results could not be reproduced for technical reasons⁷, we focused on other spectroscopic data on the Si-H surface⁸⁻¹⁰, and with our analytic theory, complemented by a kinetic Monte Carlo solution of the differential equations, and the using other SiH data we are investigating the problem anew and obtained conditions for sufficient pooling as to yield the infrared dissociation of the H₂ using an intense laser. The pooling greatly increases with high light intensity. We are preparing a paper analyzing these results and those of Sum Frequency Generation (SFG) experiments on an Si-H surface.

B. Intermittent Fluorescence in Single Particle Studies

B1. Theory of Power Law and Exponential Tail for Intermittently Fluorescing Semiconductor Nanoparticles

This area has been the subject of numerous experimental and theoretical studies for the past two decades, e.g.,¹¹⁻¹⁹. In our current work we have set up a unified theory that explains some facts for which there was no previous quantitative unified treatment, including our own earlier work, e.g.,^{15, 20-27}. Rather they described various aspects of the problem but not as whole. Key facts are that both the light and the dark periods (fluorescing and non-fluorescing periods) show a power law with a slope averaging about -1.5 for a plot of the log of the “waiting time” distribution versus the log of the time, for both the dark and the light periods, while only the bright period has an exponential tail in this plot, and the onset of the tail varies as the square of the light intensity.

In the present work we again set up a reaction-diffusion differential equation for the “structural diffusion” in the nanoparticle (“spectral diffusion”), including now both excitons and

biexcitons²⁸⁻³², to explain these and other experimental facts. In this way, we developed a theory in which the -1.5 power law aspect arises from a slow structural diffusion of the system which permits it when the initial and final states are “in resonance” (same energy), to go from light to dark or dark to light states. The exponential tail is explained in terms of the biexciton, a high energy system that doesn’t require a resonance to occur due to the formation of biexcitons. The theory also provides an explanation of why the exponential tail does not occur for the dark state.

A number of other experimental facts, such as the dependence of the tail on the square of the light intensity are also explained and predictions made. We obtained a numerical solution of the problem, but an expansion at long times provides simple and valid expressions to compare with the experimental data, such as the -1.5 power law and the exponential tail that varies as the square of the light intensity. The theory is described in a paper being prepared for publication.

B2. Theory of Intermittent Fluorescence of Single Molecules on Plane Surfaces and on Sintered Nanoparticles

In single molecule studies of injection of an electron from a photoexcited dye into a semiconductor crystal or into a film of sintered semiconductor nanoparticles^{30,31}, a power law was observed for the distribution of dark periods (dye cation periods in the case studied) for the return of the electron to the dye. When the injection is into a semiconductor with a wide band gap, the distribution of injection times also follows a power law with a slope of -1 in the rare examples studied. In this case the injection is into a trap.

In this work we set up and solved the partial differential equations describing this system (Laplace transform) and also obtained the approximate (long) times appropriate to cover the experimental observations³². With this solution it provided the answer as to when a power law for the waiting time distribution may be expected and what that power might be. When the injection is into the conduction band we obtain a power law only for the return of the electron to the dye cation but not for the injection. After a short time the log-log waiting time distribution for the return of the electron to the dye cation has a slope of -1. When the injection is into the band gap a -1 power law is predicted for both the injection and the return.

The data^{30,31} were discussed in terms of theory. A corollary was that single molecule studies for the injection can determine whether the injection is into the band gap or into the conduction band. The theory was applied to single molecule studies of systems, such as dye-TiO₂, dye-Al₂O₃, and dye-ZrO₂ systems, and to dye hole injection³³ into a p-type NiO semiconductor. An article on these results was published in *J. Phys. Chem. C*.³²

B3. A Maximum Likelihood Method for Power Law Distribution that Does Not Break Down When the Slope is Close to Unity

We formulated a general maximum likelihood estimation (MLE) method for analyzing experimental data with a power law form, with any power exponent, which does not break down for a power close to -1³⁴. It contrasts thereby with a standard literature procedure^{31,35,36} that does break down for this particular important power (it has a singularity there). Our method, which uses a sum instead of an integral, can be extended to a power law with an exponential tail and more generally to other distributions. Inasmuch as the theoretical value of the power for dye

sensitized charge recombination on surfaces of semiconductor systems, and for certain charge injection, is -1 (topic B2), the present correction to the current MLE method has immediate application to the data in these systems. The results of this research were published in *J. Phys. Chem. C*.³⁴

B4. Fundamental Theory of Organic/Inorganic Hybrid Solar Cells

In the field of solar cells we are developing equations that take account of trap states and that does not assume an equilibration of the population in those states, We have set up differential equations for photo-excitation, electron injection, migration, recombination, and electron transfer at electrodes, simplifying the problem by assuming that diffusion is fast (so converting a partial differential equation into an ordinary one). To explain an experimental observation of a “stretched exponential” recovery time in some experiments³⁷, instead of a simple first or second order recovery, we do not use a common assumption that the population in the traps is equilibrated. In this research there has been a synergy with the kinetic concepts we use here and those for equilibration that we used in the pooling study. This work is an ongoing project and will treat the older, e.g.,³⁸⁻⁴³ and newer (perovskite-like) solar cells, e.g.,^{44, 45}. The theory will be compared with theories that assume equilibration. The P.I. contributed to a chapter of J.A. Bisquert on the theory of photovoltaic solar cells.⁴⁶

B5. Sum Frequency Generation Study of Water-Air Surface

We studied a model that we used⁴⁷ for catalysis⁴⁸ of an organic (cyclo addition) reaction in a water-organic emulsion catalysis by a free (not hydrogen bonded) OH group of a water molecule at the interface) by studying experiments based^{49, 50} on Sum Frequency Generation, a surface sensitive technique. Different polarizations of the visible and infrared lasers, the infrared tuned to an absorption at 3700 cm^{-1} , the peak specific for a surface water molecule that has a free non hydrogen bonded OH group. We studied various polarizations of the SFG experiments, and calculated SFG signal intensities for each. We used the integrated intensity of the absorption peak and compared the molecular dynamics/statistical results for the observed second order susceptibility coefficient. In contrast to most other SFG theoretical studies, e.g.,⁵¹⁻⁵⁴ absolute intensities were calculated, using transition dipole moments and polarizability matrix elements obtained from non-SFG experiments.⁵⁵

C. Beyond Surface Studies

Semiclassical Evaluation of Kinetic Isotope Effects in a 13-Atom System

The semiclassical instanton approach was discussed by Dr. Maksym Kryvohuz⁵⁶, a member of the group, and applied to calculate the kinetic H/D isotope effect (KIE) of intramolecular hydrogen transfer in cis-1,3-pentadiene in a paper published in *J Chem Phys*.⁵⁷ All 33 vibrational degrees of freedom were treated quantum mechanically with a semiclassical approximation.

Nuclear quantum effects such as tunneling under the barrier and zero-point energy were automatically incorporated in the theory, and were shown to be responsible for the observed KIE in cis-1,3-pentadiene. The numerical calculations were performed using an empirical valence bond potential energy surface and compared with the previous experimental and theoretical studies. An estimate of heavy-atom $^{12}\text{C}/^{13}\text{C}$ KIE in the same system was also provided and the factors contributing to it were discussed. The method is an approximation to a more rigorous instanton method⁵⁸ with less computation needed. Its utility is being explored by Kryvohuz (now

at Argonne) in an application to enzyme catalysis. After leaving the group Kryvohuz further extended the utility of the theory by introducing on-the-fly high level electronic structure potential energy computations for the chemical reactions.⁵⁹

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